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Note

MODIFICATION OF THE HANCOCK AND SHARP "lnln METHOD" IN ORDER TO PERFORM THE KINETIC ANALYSIS OF NON-ISOTHERMAL DATA

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Hancock and Sharp [1] have developed an empirical method for discerning the kinetic law fitted by isothermal data of solid state reactions from the plots of $\ln[-\ln(1-\alpha)]$ vs. $\ln t$ for α values lower than 0.7, α being the reacted fraction at time t. These authors have observed that such plots are straight lines, the slopes of which are characteristic of the reaction mechanism. The theoretical basis of this empirical method has been stated in a very recent paper [2].

The scope of the present work is to modify the above method in such a way that permits the discrimination of the reaction mechanism of solid state reactions from non-isothermal data obtained at a linear heating rate which, as known, can be described by the kinetic equation

$$g(\alpha) = \frac{1}{\beta} \int_{T_0}^{T} A \exp(-E/RT)\,dT \tag{1}$$

or

$$\ln g(\alpha) = \ln \frac{1}{\beta} + \ln \int_{T_0}^{T} A \exp(-E/RT)\,dT \tag{2}$$

where β is the heating rate, A is the pre-exponential factor of Arrhenius, E is the activation energy, T is the absolute temperature and $g(\alpha)$ is a function depending on the reaction mechanism.

It has been stated in a previous work [2] that for α values in the range 0.05—0.7, the $g(\alpha)$ functions of the different kinetic laws describing solid state reactions are correlated with $\ln[-\ln(1-\alpha)]$ through the expression

$$\ln g(\alpha) = \frac{1}{n} \ln[-\ln(1-\alpha)] + a \tag{3}$$

where n and a are constants. The values of n calculated in ref. 2 for the different reaction mechanisms of solid state reactions are included in Table 1.

From eqns. (2) and (3) we get

$$\ln[-\ln(1-\alpha)] = n \ln \frac{1}{\beta} + n \ln \int_{T_0}^{T} A \exp(-E/RT)\,dT - na \tag{4}$$

TABLE 1

Values of n calculated in ref. 2

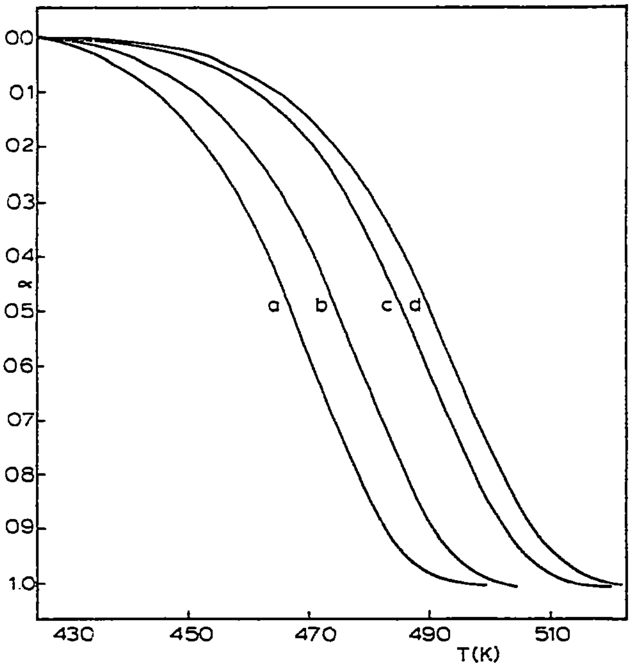
Mechanism	n	*Mechanism*	n
Zero order (R_1)	1.18	D_2	0.56
R_2	1.09	D_3	0.53
R_3	1.06	D_4	0.55
F_1	1.00	A_2	2.00
D_1	0.59	A_3	3.00

Hancock and Sharp's symbols [4] have been used.

which, for α values taken at a given temperature from a series of α—T curves obtained at different heating rates, becomes

$$\ln[-\ln(1-\alpha)] = n \ln\frac{1}{\beta} + \text{const.} \tag{5}$$

Therefore, the plot of the left-hand side of eqn. (5) vs. ln $(1/\beta)$ yields a straight line whose slope, n, allows the discernment among reactions with the rate determining step controlled by diffusion (D_i, D_2, D_3, D_4), movement of phase-boundary (R_1, R_2, R_3, F_1), or nucleation and nuclei growth (A_2, A_3).



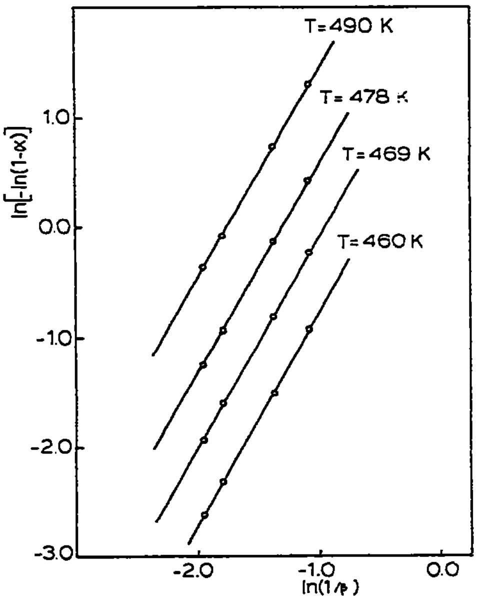


Fig. 1. Theoretical α—T curves obtained at differerent heating rates by assuming an A_2 mechanism and the following kinetic parameters: E = 30 kcal/mole^{-1}; $A = 10^{12}$ min^{-1}. (a) β = 3°C min^{-1}; (b) β = 4°C min^{-1}; (c) β = 6°C min^{-1}; (d) β = 7°C min^{-1}.

Fig. 2. Plot of data taken from Fig. 1 in agreement with eqn. (5).

In order to test the above method we have constructed the series of α—T curves included in Fig. 1 by assuming an Avrami—Erofeev mechanism with $n = 2$, A_2 (i.e. $g(\alpha) = [-\ln(1-\alpha)]^{1/2}$) and kinetic parameters $E = 30$ kcal/mole^{-1}, $A = 10^{12}$ min^{-1}. The Arrhenius equation has been integrated by means of the 4th degree rational approach proposed by Senum and Yang [3], which involves an error $<10^{-3}$%.

The kinetic analysis of the data taken from Fig. 1 at several given temperatures has been carried out by means of eqn. (5), as shown in Fig. 2. The slopes of the straight lines obtained in this way are $n = 2$, as would be expected from Table 1.

In summary, we can conclude that the method described in the present paper is an easy and quick way of distinguishing the actual mechanism of a solid state reaction.

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